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Research article

Secondary pyrolysis pathway of monomeric aromatics resulting from oxidized β-O-4 lignin dimeric model compounds

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ABSTRACT

Thermal reactions of six monomeric aromatics (typical primary pyrolytic products of β-O-4 lignin dimers) were studied in a closed ampoule reactor (N_2/400–600 °C/120 s) to obtain the information on secondary pyrolysis pathway of products. The result showed that the secondary pyrolysis of monomeric aromatics mainly included two pathways: polymerization and side-chain-conversion, and the polymerization were more competitive under all the test conditions. The amount of -OCH_3 group was an essential factor on the reactivity of monomeric aromatics, and the introduction of -OCH_3 group enhanced the conversion of monomeric aromatics. In the presence of -CHO group on the p-position of aryl-OH, the removal of -CHO group was major side-chain-conversion reaction during the pyrolysis process. Adding the amount of -OCH_3 group was beneficial for promotion the breakage of aryl-CHO bond; instead, when the p-position of phenolic hydroxyl group was -$COCH_3$ group, the cleavage of aryl-$COCH_3$ bond was inhibited, where radical induced rearrangement of aryl-OCH_3 group into aryl-CH_3 group firstly happened and as the major side-chain-conversion reaction. Besides, new reactant intermediates, which were directly formed via side-chain-conversion of initial samples, could further decompose to other aromatic monomers, and influenced the products distribution and selectivity via a series of reactions.

1. Introduction

Aromatic chemicals are the important raw materials in the chemical industry and mainly are obtained from fossil resources. Due to the depletion of fossil fuels and severe environmental issues, the utilization of biomass resources for aromatic chemicals has gained wide spread attention [1]. Lignin is an aromatic biopolymer which occurs as an integral cell wall component of all vascular plants including the herbaceous varieties, constituting the largest abundant aromatic biomass available on earth [2]. The macromolecular structure suggests that, under controlled degradation it can be considered as an alternative raw material for the low molecular weight aromatics [3]. Further, pyrolysis has been projected to be an important thermochemical method for obtaining the high-added value aromatic chemicals such as vanillin via selective degradation of lignin [4]. However, the structural complexity of lignin in wood tissues seriously hinders in depth studies of its degradation pathway, resulting in the relatively low yields and the bad selectivity of monomeric aromatics.

As a natural complex aromatic polymer, lignin is comprised of three phenyl propane units (*p*-coumaryl, guaiacyl and sinapyl units), and these units differ in the number of -OCH_3 groups [5]. Sinapyl unit has two -OCH_3 groups, guaiacyl unit has one -OCH_3 group, and *p*-coumaryl unit has none. Generally, these three phenyl propane units are linked by various chemical bonds (β-O-4, α-O-4, β-1, 5-5, etc.) [6]. Hereinto, the β-O-4 linkages account for approximately 48–60% of the total linkages in lignin depending on the various biomass types [7], and significantly influence the chemical and physical properties of lignin. Over the past few decades, β-O-4 lignin models were generally used to investigate the pyrolysis mechanism instead of lignin [8–11], due to the simple structures and similar product distributions. In previous reports [12–14], it was clear that thermal-decomposition of lignin included a complex reaction pathway where competitive fragmentation and condensation reactions occurred. Klein proposed that lignin pyrolysis occurred by free radical chemistry [12]. Britt and co-workers [13] further confirmed that the thermal-decomposition of lignin principally followed a multiple, parallel radical and rearrangement pathway. Ragauskas and co-workers [14] summarized the two main proposed routes for pyrolysis of lignin model compounds, including free-radical reactions and concerted pericyclic reactions. Overall the literature had primarily postulated free-radical reaction mechanisms in which the radicals were generated by homolytic cleavage of the relatively weak aryl C—O bond and then were involved in hydrogen abstraction, dimerization and

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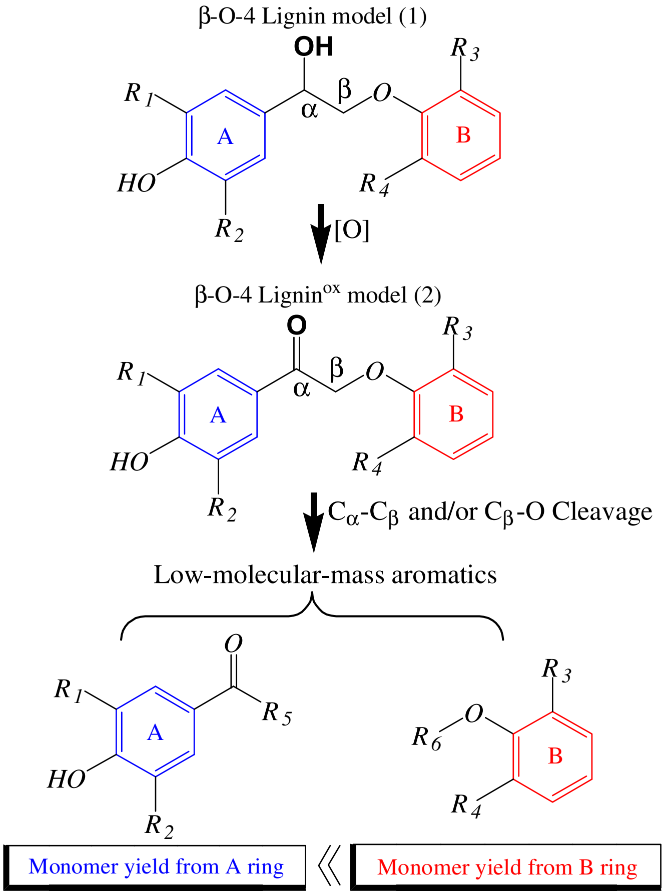


Scheme 1. Typical scheme of lignin oxidation depolymerization. (R_1–R_4 = CH_3O or H; R_5, R_6 = CH_3 or H).

oligomerization. Nevertheless, even in this case, the known thermochemical methods typically afford ill-defined products in low monomeric aromatics yields (that is less than 10–20%) [15–17]. One of important reason was that most of research groups focused on the original fragmentation pathway, while ignoring the study of secondary pyrolysis routes. Exactly, the latter might play an important role in lignin pyrolysis process.

With more and more research available, it was found that the utilization reported by the methods in lignin depolymerization system, affording one-step routes for β-O-4 bonds cleavage was a significant challenge. More recently, several groups [18–20] have developed an elegant approach to catalytically transform lignin to structurally defined monomeric aromatics. Exemplified by the experimentally used β-O-4 lignin dimer model, Scheme 1 recapitulated their strategy. The method broke the β-O-4 linkage through two stages: (1) aerobic oxidization of the C_α alcohol to a carbonyl group (see Scheme 1, β-O-4 lignin model → β-O-4 lignin^{ox} model), (2) cleavage of the C_β—O bond or/and C_α—C_β of β-O-4 lignin^{ox} model via pyrolysis. Notably, the most attractive appeared to be that second stage was a facile reaction process, and could obtain higher yields of aromatic monomer compared to the previously reported. Our laboratory also investigated the pyrolysis behavior of β-O-4 lignin^{ox} model [21]. It was demonstrated that oxidation of the benzylic position of β-O-4 lignin models to C_α=O group resulted in easier the C_α—C_β bond cleavage and, as a result, allowed access to high-value aromatic monomer. Meanwhile, the yield and selectivity of monomeric aromatics (see Scheme 1) was very interesting. Cleaving the C_α—C_β or C_β—O bond yielded different ratios of oxidized monomeric products from the ring A, i.e., 4-hydroxy-acetophenone, 4-hydroxy-3-methoxy-acetophenone and 4-hydroxy-3, 5-dimethoxy-acetophenone, along with phenol, 2-methoxy-phenol and 2, 6-dimethoxy-phenol from the ring B. The reaction stoichiometry of dimer meant that the moles yield of products from ring A should be equimolar with that from ring B. However, based on the past experimental results, it was found that the mole yield of monomeric aromatics from ring B was significantly more than that from ring A [21]. Hence, we speculated that the decrease of the products from ring A could be the crux evidence of the secondary pyrolysis of products.

In the present work, these reaction pathways of β-O-4 lignin dimeric model compounds were further elucidated by explaining the transformation and/or degradation routes of monomeric aromatics (typical primary pyrolysis products of ring A). Considering to the types of lignin structure units and the cleavage position (C_β—O or C_α—C_β bond) of β-O-4 lignin^{ox} dimers, the influence of -CHO, -$COCH_3$ and -OCH_3 groups on the secondary pyrolysis behavior of products was investigated. The results might give insight on pyrolysis mechanism of lignin, and help to regulate and control the experiment condition for selectively increasing the yield of aromatic monomers.

2. Materials and methods

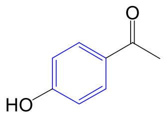
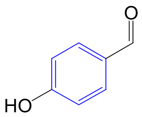
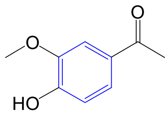
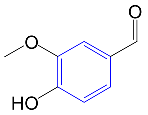
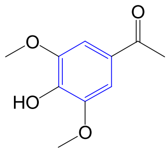
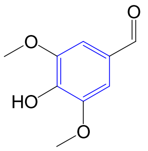
2.1. Materials

Six types of monomeric aromatics obtained from ring A (see in Table 1) were used in this study: (1) 4-hydroxy-acetophenone (Aldrich, 98%) referred to as H-Ketone; (2) 4-hydroxy-3-methoxy-acetophenone (Aldrich, 98%), referred to as G-Ketone; (3) 4-hydroxy-3, 5-dimethoxy-acetophenone (Aldrich, 98%), referred to as S-Ketone; (4) 4-hydroxy-benzaidehyde (Aldrich, 98%), referred to as H-Aldehyde; (5) 4-hydroxy-3-methoxy-benzaidehyde (Aldrich, 98%), referred to as G-Aldehyde; (6) 4-hydroxy-3, 5-dimethoxy-benzaidehyde (J & K, 98%), referred to as S-Aldehyde. Furthermore, monomeric aromatics (1)–(3) and (4)–(6) were selected as the products via cleavage of the C_β—O bond and C_α—C_β band, respectively. All chemicals were used without further purification.

2.2. Typical pyrolysis experiments

Fast pyrolysis of monomeric aromatics was carried out with a tubular reactor using quartz U-tube. The detail of apparatus was described in the past report [22]. About 100 mg sample was added into the quartz U-tube as a methanol solution, and then the solution was evaporated in vacuum in an upright position. After exchanging the air inside the tube with N_2, the tube was sealed at atmospheric pressure. Pyrolysis was conducted by inserting the whole ampoule into a muffle furnace which had been preheated to a desired temperature at 400, 450, 500, 550 or 600 °C. After pyrolysis for 2 min, the U-tube was immediately removed

Table 1
Monomeric aromatics used in this study.

Structural formula	Abbreviation	Structural formula	Abbreviation
	H-ketone		H-aldehyde
	G-ketone		G-aldehyde
	S-ketone		S-aldehyde